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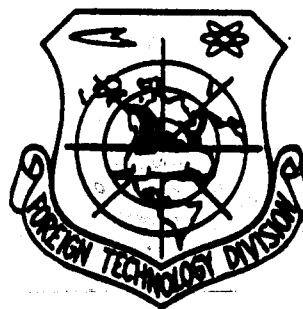
# FOREIGN TECHNOLOGY DIVISION



ABOUT THE SERIES SPECTRA OF THE ELEMENTS  
OXYGEN, SULFUR, AND SELENIUM

by

C. Runge and F. Paschen



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# ABOUT THE SERIES SPECTRA OF THE ELEMENTS OXYGEN, SULFUR, AND SELENIUM

by C. Runge and F. Paschen

## INTRODUCTION

Since the investigations of Plücker and Hittorf it has been known that the discharge of electricity in a gas will produce different spectra, depending on the kind of gas present and on its pressure. Plücker and Hittorf observed continuous band spectra in a series of gases exposed to the discharges of an induction apparatus. When a Leyden jar and a spark gap were connected to the circuit, the continuous band spectrum vanished and gave way to a line spectrum. Schuster<sup>1</sup>, working with oxygen, demonstrated that under the conditions which produce continuous band spectra with the gases investigated by Plücker and Hittorf, oxygen produces a line spectrum in addition to the continuous band spectrum visible in the vicinity of the cathode. Both the line spectrum and the continuous band spectrum vanish and give way to a new line spectrum when a Leyden jar and a spark gap are connected to the circuit. Schuster named the first line spectrum the "compound" line spectrum of oxygen and observed that it consisted of four lines. Paalzow and H. W. Vogel<sup>2</sup> made a more thorough investigation of this "compound" line spectrum, albeit using a smaller dispersion. Until now, the most complete investigation of the compound line spectrum has been that of Piazzzi Smyth<sup>3</sup>, whose work, it appears, has attracted too little notice. His measurements have not been included in the catalogue of the British Association, nor in the Index of Spectra compiled by Watts, most probably because he had the unfortunate idea of using the English inch as his basic unit of measurement, and provided us only with a drawing of the spectrum from which only the reciprocal values of the wavelengths as expressed in inches can be deduced. We have also made an investigation of the compound line spectrum, and can confirm the results obtained by Piazzzi Smyth, expanding and confirming them in several respects. At the same time we have investigated the chemically related elements sulfur and selenium and have found that under certain conditions they produce a spectrum analogous to the compound line spectrum, an effect which to our knowledge has not been noted

1) Schuster, Phil. Trans. 170, 1879.

2) Paalzow u. H. W. Vogel, Wied. Ann. 13, 1881.

3) Piazzzi Smyth, Trans. Edinb. Roy. Soc. 22, 1884.

previously. It is worth noting that these spectral lines, some of them quite strongly marked, have somehow escaped detection until now; at the same time it strikes us as not unlikely that some of the lines of unknown origin that have been observed in the sun and the stars can be linked with known elements if those elements can be made to luminesce under other conditions.

The three spectra of oxygen, sulfur, and selenium show a great regularity of structure. The lines are grouped in series which follow the laws given by Rydberg, and Kayser and Runge. A comparison of the three spectra with one another also shows a marked regularity. As the atomic weight increases, the spectrum, on the whole, moves towards larger wavelengths, a pattern similar to that observed in the series spectra of other groups of chemically related elements.

#### § 1. THE APPARATUS

Geissler tubes were set up in the manner described in our investigation of the spectrum of helium.<sup>1</sup> The only difference was that the tubes remained connected to the vacuum pump throughout the experiments. We did not affix the tubes in such a manner that they could be melted off. They had to be constantly handled, heated, emptied, and flushed with oxygen if one wanted to retain a sufficiently bright and clear spectrum. The light emanating from the small window in the tube was focused on the aperture of the spectral apparatus with a quartz lens. In addition to a small pocket spectroscope, used to control the operation of the tubes, we used a small Rowland-type concave grid with a radius of curvature of 1 meter, with a  $4 \times 8 \text{ cm}^2$  grooved surface having ca. 600 grooves/mm, as well as a larger Rowland-type concave grid having a radius of curvature of 6.5 meters,  $5 \times 15 \text{ cm}^2$  grooved surface and ca. 800 grooves/mm. The Geissler tubes were connected to the vacuum pump by a vertical cutoff, enabling us to turn the tubes on a vertical axis without disturbing the vacuum. This gave us a choice of spectra through either the smaller grid or the larger one. For this purpose, the centers of curvature, the aperture, and the grids were all set up on a single plane. The smaller of the concave grids gave a significantly brighter spectrum than the larger concave grid, but it had only 2/17 of the larger grid's dispersion.

1) Runge u. Paschen, *Astrophys. Journ.* 3. Jan. 1896.

With the smaller grid, we obtained 17 angstroms/mm in the first order, while the larger one gave us close to two. At the same time, the smaller dispersion is by no means a disadvantage for many purposes, since it allows a rapid overview of the entire spectrum. We did not set up the grids according to Rowland's specifications. In particular for the smaller grid a different setup proved more suitable. The aperture and the grid were placed in a fixed position on a mirror glass plate blackened with lamp-black. When the aperture lies on a circle drawn around the focus of the convex mirror formed by the grid at a distance of half the radius of curvature, the spectrum is found on the same circle. There we prepared a solid wooden frame onto which a Schleussner-type photographic film was attached by means of rubber bands. The wooden frame was bent in such a manner and affixed to the glass plate so that the whole spectrum was correctly projected onto the film. A cover constructed of wood and cardboard and set over the entire apparatus guarded against outside light. This setup is also to be recommended for direct visual observations. We placed a scale, calibrated mechanically and copied onto photographic paper with intervals of 10 angstroms marked, on the wooden frame. The edge of this strip of paper could be pushed into the spectrum, enabling the observer to read the wavelengths of the spectrum rapidly within an accuracy of about one or two angstroms. For some observations speed is more vital than accuracy, such as when the spectrum is changing rapidly and one desires to know which lines appear simultaneously. The whole spectrum was not longer than 25 cm, so that it was not necessary to leave one's seat in order to survey the entire spectrum at a glance. This setup is also suited for exact visual measurements. For this we affixed a microscope with weak magnification to the runners of an Abbe-type comparator, the microscope being equipped with crosshairs. One could then read off the displacement of the microscope on the comparator scale when the crosshairs were centered on a given spectral line. One could then interpolate from the wavelengths of known spectral lines the wavelengths of unknown spectral lines lying between them. We used this technique to measure the red lines of our spectra. Photographic measurements in this case would not have been practical, due to the weak sensitivity of the photographic emulsions sensitive to red. For purposes of comparison we used, in part,

the red lines of the solar spectrum as measured by Rowland, and in part lines from the spectra of oxygen and argon which had been calibrated against the solar lines. For the red portion of the spectrum, the spectrum of argon is especially useful for purposes of comparison, since it contains an adequate number of bright red lines. Of course one must first make an exact measurement of the argon lines; the extant figures supplied by Crookes, Kayser, Eder, and Valenta are not exact enough in this part of the spectrum. We will publish our measurements of the argon lines in a separate monograph. For the large grid, we also have used a setup that reduced dispersion by about one half. A six-inch refractor belonging to the Geodetic Institute of the Polytechnic School was set up so that the aperture coincided with the crosshairs, and the light coming through the aperture fell parallel on the concave grid. The spectrum then lies on a circle the diameter of which is equal to the line connecting the grid with its focal point. This increases the brightness by a factor of four, and gives the advantage that in the vicinity of the focal point the image of the aperture is, as is shown by the theory of grids, not astigmatic,

and thus the imperfections of the aperture and of its adjustments are obviated. This setup is recommended for laboratories where lack of space makes a Rowland-type arrangement with a large grid impracticable. In our method, the room need be no larger than 4 meters in length. In order to obtain the greatest possible brightness in visual observations, we have used a cylindrical lens as magnifying glass, by setting its axis parallel to the lines. This way magnification is limited to the direction of the spectrum, which after all is the main consideration, and not in the direction

of the lines, and more light is concentrated on a given area of the retina than if one magnified in both directions. Naturally this is only applicable when the lightrays projected from one point on the line do not fill the pupil of the eye in a vertical direction. In the case of the large grid, however, they are far from meeting this condition. The grooves are 5 cm long, and without the refractor the spectrum is ca. 650 cm removed from the grid, while with the refractor this distance is reduced to 325 cm. The angle formed by the rays from one point on the line is equal to 1:130

or 1:65. When an ordinary magnifying lens is used, e. g. one having a focal length of 3 cm, the lightrays from a given point on a spectral line will have a circular diameter of 0.23 mm or 0.46 mm when they reach the pupil of the observer's eye, while the pupil itself measures 2 - 4 mm in diameter.

## § 2. THE COMPOUND LINE SPECTRUM OF OXYGEN

In order to obtain the purest possible spectrum for oxygen, we employed the methods described by Paalzow and H. W. Vogel.<sup>1</sup> Using a U-shaped curved tube, we connected both arms of the tube to a mercury vacuum pump. We filled the tube with concentrated  $H_2SO_4$  and inserted platinum wire electrodes which then were used to generate hydrogen in one arm and oxygen in the other by running a current through the apparatus. From the one arm of the U-shaped tube the gas was sucked directly into the vacuum pump, while the gas from the other arm first passed through a Geissler tube, then through a U-shaped bend in the tube filled with a solution of potassium bichromate in concentrated  $H_2SO_4$  and then passed into the tube connecting the other arm to the pump (see illustration 1). The chromic acid has the purpose of keeping carbon compounds from valve lubricants away from the Geissler tube. By this means it is not difficult to avoid the carbon oxide bands that so easily form in the spectrum of a Geissler tube. When the tube is heated with a Bunsen burner and a stream of oxygen is passed through it, with the pump operating continuously, the tube will show a pure oxygen spectrum; only the hydrogen lines  $H_\alpha$ ,  $H_\beta$ ,  $H_\gamma$ , etc. remain, and we have made no effort to remove them. Mercury lines also appear easily, as do the sodium lines  $D_1$  and  $D_2$  when the capillary becomes hot. All these lines are normal and desirable.

In other parts of the tube, the bands observed by Schuster were visible, and a whole series of the lines of the spark spectrum, even though no Leyden jar or spark gap had been connected to the circuit. In the capillaries the lines of the compound line spectrum appeared.

<sup>1</sup> Paalzow u. H. W. Vogel, Wied. Ann. 13. p. 336. 1931.

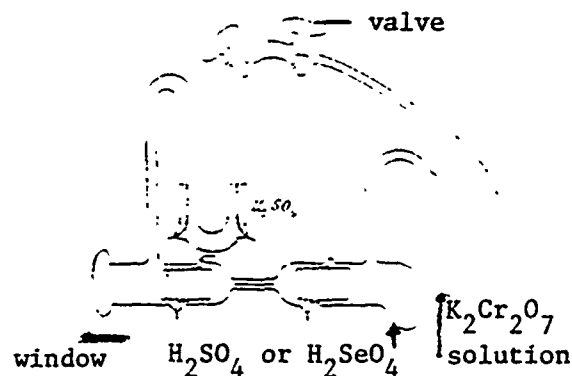


ILLUSTRATION 1.



When a Leyden jar and a spark gap are switched into the circuit, the lines of the compound line spectrum dim and become less distinct. Simultaneously the lines of the spark spectrum appear much more strongly in the capillaries, while the bands vanish. The wavelengths of the compound line spectrum are:

A	B	C	D	E
Wellenlänge bezogen auf Rowlands Normale	Mittlerer Fehler	Zahl der Be- obachtungen	Inten- sität	Bemerkungen
2983.05	0.01	4	6	Deslandres Nr. 2983.5
3092.588	0.008	3	7	gegen Eisennormalen Deslandres: 3092.0
3823.714	0.013	2	7	gegen Eisennormalen Deslandres: 3823.8 <u>a</u>
3925.22	0.04	3	6	
3990.11	0.07	3	2	
3947.490			10	
3947.081	0.010	3	7	Deslandres: 3947.2
3947.739			4	
4004.775	0.009	3	3	gegen Eisennormalen Deslandres: 4005.
4017.55	0.01	4	7	
4022.04	0.01	3	7	
4030.48	0.008	3	7	
4065.198	0.010	3	10	gegen Eisennormalen Schuster: 4067. <u>b</u>
4022.051				
4030.70				
4070.070	0.11	2	2	

KEY TO TABLES ON pp. 6-7:

- A Wavelength related to Rowland's norms  
B Mean error<sup>1)</sup>  
C No. of observations  
D Remarks

a measured against Deslandres iron norm...

b measured against Schuster iron norm...

c in three exposures the two lines couldn't be differentiated; in these the mean is calculated at 4654.66, the mean error at 0.05

d in four exposures the two lines could not be differentiated; in these the mean is calculated at 4772.96, the mean error at 0.015

e not separated in three exposures; mean 4802.29, mean error 0.08

f measured against Piazzzi Smyth iron norm...

g indistinct

h against iron norms; a weak companion found on side of smaller wavelengths

i against argon lines

j against argon lines and solar lines

k the mean error of the mean is 0.015; the distance between the two lines is less, precisely because it was hard to see them when the aperture was set sufficiently narrow to separate them

<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u> Bemerkungen
Wellenlänge bezogen auf Bowditch's Normale	Mittlerer Fehler	Zahl der Be- obachtungen	Intensität	
4577.54	0.00	2	3	
4589.16d	0.00	2	2	
4590.07	0.08	2	3	
4654.41		1	2	Bei drei Aufnahmen konnten die beiden Linien nicht getrennt werden. Bei diesen giebt das Mittel 4654.56, mittl. <u>c</u> Fehler 0.05
4654.74		1	3	
4671.54	0.03	4	1	
4672.01	0.04	3	3	
4673.78	0.04	4	3	
4772.72	0.02	2	3	Bei vier Aufnahmen konnten die beiden Linien nicht getrennt werden. Bei diesen giebt das Mittel 4772.99, mittl. <u>d</u> Fehler 0.015
4773.7	0.02	2	1	
4773.84	0.01	6	3	
4801.28	0.12	2	2	Bei drei Aufnahmen nicht getrennt. Mittel 4802.29, mittl. Fehler 0.08 <u>e</u>
4802.28	0.10	2	3	
4803.18	0.03	3	4	
4867.55	0.04	3	4	Piazzi Smyth: 4864.9
4905.04	0.04	3	3	gegen Eisennormalen .. .. 4905.0 <u>f</u>
4921.14	0.01	3	6	.. .. 4921.1
4970.05		1	1	unscharf <u>g</u>
4970.70		1	1	
5018.56	0.04	2	2	bei 7 Aufn. n. getrennt .. .. 5018.30 <u>h</u>
5019.52	0.07	2	4	
5020.21	0.01	13	5	ML 5019.28 mittl. F. 0,2 .. .. 5017.4
5037.34	0.5	3	2	.. .. 5018.53
5047.55	0.1	4	2	unscharf <u>g</u>
5130.70	0.07	9	3	
5146.23	0.08	3	5	gegen Eisennormalen Piazzi Smyth: 5145.15 <u>f</u>
5275.25	0.04	7	4	
5299.17	0.03	3	5	" " <u>b</u> <u>f</u>
5329.102			6	Schuster <u>b</u> <u>f</u> Piazzi Smyth 5329,293 5329,77 5329,774 5329,827 5330,44 5330,835 5330,798 5331,44
5329,774	0,01	3	7	
5330,835			10	
5405,08	0,10	6	8	
5408,80	0,04	7	4	
5410,97	0,03	7	8	Piazzi Smyth: 5407,94

1) Schuster, Astrophysical Journal 5. p. 163.

A	B	C	D	E Bemerkungen	
Wellenlänge bezogen auf Hörwala's Normalen	Mittlerer Fehler	Zahl der Be- obachtungen	Intensität		
5435.371			5	Piazzi Smith: 5435.00	
5435.905	0.015	3	6	gegen Eisennormalen	5436.15 <u>f</u>
5437.041			8	.. .. 5437.25	
5512.92d	0.02	3	5	gegen Eisennormalen.	
				schwacher Begleiter	
				liegt auf der Seite der	<u>h</u>
				klein. Wellenlängen	.. .. 5511.00
5535.111	0.04	3	6	gegen Eisennormalen.	<u>f</u>
				schwacher Begleiter	<u>h</u>
				auf der Seite der	.. .. 5535.15
5551.52	0.04	2	5	gegen Eisennormalen	
5555.711	0.02	3	6	gegen Argonlinien.	<u>1</u>
				schwacher Begleiter	<u>h</u>
				auf der Seite der	.. .. 5552.55
				klein. Wellenlängen	.. .. 5553.14
5592.57		1	3	.. .. 5590.31	
5595.70	0.15	3	4	gegen Argonlinien <u>1</u>	7
5640.382	0.03	3	2	.. .. 5642.32	
5640.514		3	7	.. .. 5650.50	
5650.175		3	7	.. .. 5650.72	
5650.772	0.015	7	5	gegen Argonlinien u.	.. .. 5650.41
5655.115			10	gegen Sonnenlinien	.. .. 5657.75 <u>1</u>
6256.51	0.05	1	1		
6261.55	0.03	1	3		
6264.75	0.00	1	1		
6267.00	0.04	1	1		
6453.900			6	gegen Argonlinien <u>1</u>	.. .. 6455.04
6454.726	0.015	5	7	.. ..	6455.56
6456.257			9	.. ..	6457.41
7002.45	0.18	4	4	.. ..	6998.20
7254.32	0.13	1	2	.. ..	7273.51
7772.26	0.07	5	10		
7774.30			8	0.15 ist der mittlere Fehler des Mittels. Der	
7775.97	0.15	8	6	Abstand der beiden Linien ist weniger	
				genau, weil es schwer war, sie noch zu sehen, <u>k</u>	
				wenn der Spalt eng genug war, um sie	
				zu trennen Piazzi Smyth: 7776.36	

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NOTES TO TABLE ON p. 6:

- 1) The figures given here for mean error are not very meaningful in cases where the number of observations is small, since it is possible that in a small number of observations the deviation from the mean can also be quite small. Nevertheless we thought it right to include the mean error since when taken as part of the whole picture, they give an objective representation of the accuracy of the results obtained.
- 2) These measurements are not in relation to Rowland's norm. Were that the assumed norm, our figures would increase by a factor of 1:7000.
- 3) The mean error for these lines is derived from a comparison of measurements taken from photographic exposures made using the smaller grid, where the three components do not appear separately. The intervals between the components were determined by using the larger grid. The mean error, therefore, refers to the point of greatest intensity of the three merged lines. This was found by reference to iron norms at 3947.572. The wavelengths of the three components were then determined in such a way that they would show the intervals measured by using the larger grid, with their center of gravity lying at 3947.572 when the strongest line was counted four times, the second strongest twice, and the weakest line counted once. To a point this is an arbitrary assumption. It is quite possible that the point of greatest intensity is determined primarily by the first line. In that case all three components should have larger wavelengths.
- 4) d means doubled.

The triple red line at 777 was determined by reference to iron lines of the second order. Since these could not be compared visually, we attached a number of fine wires to the camera in positions on either side of the red line and parallel to it, measured the position of the triple red line in relation to the wires, and then determined the position of the wires relative to the iron lines of the second order by making photographic exposures of the iron spectrum preceding and following the oxygen observations. During the procedure the wires were placed next to but not touching the photographic plate itself. By comparing exposures taken before and after the experiment, we were able to assure ourselves that the position of the wires had not been disturbed. In addition to the lines listed in our table we also observed some others which we take to be oxygen lines of the compound spectrum. These, however, were read only from the paper scale, and are accurate only within one or two angstroms:

6107 int. 2 Piazzzi Smyth 6103  
 7157 int. 1  
 7454 int. 1

The measurements by Piazzzi Smyth listed in our table are taken from his drawing<sup>1</sup> and converted to Rowland's scale, by which means we brought Smyth's figures for  $H_{\alpha}$ ,  $D_1$ , and  $D_2$  into the best attainable correspondence with Rowland's figures. His measurements when taken as an absolute indication are by no means remarkable. Taken as a relative indication, they are very good indeed for his time. A few weak lines on Smyth's list, which we have not found in our observations and which we assume are not oxygen lines, have been excluded from our table. Piazzzi Smyth was the first to have observed and measured three times the lines observed by Schuster, and he was the first to have discovered three additional lines of the same structure. It also did not escape his attention that these six triplets are not only of the same structure, which characterizes them,<sup>2</sup> but also that they form a regular system when taken as a whole. Had the laws of series been known at that time, he would have recognized that the oxygen triplets form two subseries converging on a single point. In each instance

1) Piazzzi Smyth, Trans. of the Roy. Soc. of Edinburgh 32. 1884.

2) Piazzzi Smyth sagt sehr richtig. The characteristics of an Oxygen triplet are so peculiar and so closely adhered to in every instance, that I have been able in some tubes swarming with lines of impurities to pick out an Oxygen triplet as easily as one would distinguish in a crowd of civilians, a soldier with cross belts and scarlet coat.

he takes one triplet of a series with a triplet from the other series and observes that they converge, pair to pair.<sup>1)</sup>

NOTE 1) As we were in the final stages of our work, Schuster informed us by letter that he had found that the six triplets (also observed by Piazzzi Smyth) form two subseries, for which he had calculated formulas.

We were also able to follow one of the series further through three additional triplets, for which further details are supplied below.

The triplet in the extremity of red at 777 was also discovered by Piazzzi Smyth, but he did not separate it. When one considers the lack of sensitivity of the human eye for this portion of the spectrum, one arrives at the surmise that this triplet must have a relatively high intensity. Probably it contains by far the strongest lines of the compound line spectrum. This triplet is especially interesting since its three lines, as far as can be judged, occur with the same relative intensities among the Fraunhofer lines.<sup>2</sup> In Higg's Atlas of the Solar Spectrum, these lines lie at 7772.20, 7774.43, and 7775.62, of which the first line is the strongest and the last the weakest. The deviations from our measurements are within the range of observational error. It must be taken into consideration that in our observations the mean of the two weaker components is much better determined than is their interval, since it was difficult to see them with the narrow aperture, while they merged with the larger aperture. The mean of the two components is 7775.14 and corresponds well with the mean 7775.02 of the lines of Higg's atlas. Schuster and Piazzzi Smyth already observed that the lines of the compound line spectrum occur among Fraunhofer's lines. But their data were not exact enough to allow for firm conclusions. Now Rowland has made such exact measurements of Fraunhofer's lines that we had to demonstrate each of the components of our triplets individually among them. This showed that the other oxygen lines, according to our measurements, could not be found among Fraunhofer's lines, or could not be demonstrated with certainty. The Fraunhofer lines with which they could be identical were, when found, so weak and surrounded so thickly by other weak Fraunhofer lines that a correspondence within the limits of observational error is meaningless. In the following

2) Vgl. Runge u. Paschen, Oxygen in the sun Astrophysical Journal 4. Dec. 1896.

table we list the strongest of the oxygen lines alongside Rowland's<sup>1)</sup> measurements of the adjacent Fraunhofer lines and those of the chromosphere.

<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>G</u>	<u>H</u>	<u>I</u>
Sauer- stoff linien	Mittel- Fehler	Inten- sität	Fraun- hofer'sche Linien	Inten- sität	Ele- ment	Linien der Chromo- sphäre	Häufig- keit	Inten- sität
			3892.498	0000				
3892.59	0.0034	7	3892.575	0000				
			3892.768	0000				
3892.77	0.02	7	3892.877	4	Mn. Cr			
			3892.893	0	"			
			3947.300	00				
3947.50		10	3947.322	2				
3947.58	1)	8	3947.675	4	Fe			
3947.78		6	3947.830	1				
			3947.918	2	Ti			
3954.73	0.02	8	3954.680	2	NiMn			
			3954.857	1	Fe?			
			4368.291	0				
4368.47	0.01	10	4368.462	0	Ni			
			4368.629	000				

1) Rowland, Preliminary table of Solar Spectrum Wavelengths. Astrophysicah Journ. 1-5.

2) Cf. Note 1, p. 647 (p. 8 of translation)

3) Cf. Note 3, p. 647 (p. 8 of translation)

KEY TO TABLES ON pp. 11-12:

- A oxygen lines
- B mean error
- C intensity
- D Fraunhofer lines
- E intensity
- F element
- G lines of the chromosphere
- H frequency
- I intensity

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A	B	C	D	E	F	G	H	I
Spektrallinien	Mittl. Fehler	Intensität	Fraunhofer'sche Linien	Intensität	Element	Linien der Chromosphäre	Häufigkeit	Intensität
			5329.000	0000		5329.7	3	2
5329.16		6	5329.320	0	Cr	5329.4	1	2
5329.77	0.01	7	5329.575	0	Cr			
			5330.170	2	Fe	5330.1d	5	2
5330.54		10	5330.748	000				
			5331.377	0000				
			5435.060	0000				
			5435.240	000				
5435.37		7	5435.325	000				
			5435.700	000				
5435.87			5435.800	000				
			5436.71	2	Ni			
			5436.825	000		5436.8	2	
			5436.841	000				
			5436.855	1	Fe			
			5436.856	0000				
			5436.892	1	Fe			
5437.04		8	5437.085	000				
			5437.300	000	Ni?			
5437.56	0.03	7	5437.245	0				
			5437.280	0000	Atm.			
5437.29		7	5437.290	000				
			5437.400	000				
5437.50		8	5437.500	000				
	0.018		5437.450	0000				
			5437.680	000				
			5437.945	3	Fe			
			5438.130	0000				
5438.42		10	5438.350	000				
5438.90		6	5438.815	0000				
5454.76		7	5454.850	0000	Atm.			
			5455.230	0	Co			
	0.015		5455.455	0000		5456,6d	15	2-10
			5455.820	2	Ca			
			5456.070	0000				
5456.29		9	5456.283	0000				
			7001.510	00				
7002.48	0.13	4	7002.385	00	Atm.			
			7002.870	0000				
			7253.493	1	Atm.			
			7254.002	1	Atm.			
7254.32	0.13	2	7254.576	0000				
7772.26	0.07	10	7772.20	3		Higg's		
7774.30		8	7774.43	2		Atlas		
7775.07	0.13	8	7775.02	1				

1) Schuster has pointed out the close correspondence btw. the two green triplets and lines of the chromosphere. Astrophys. Journ. 5. p. 163



After 777 the strongest lines are the lines of the triplets at 3947 and at 616, and the line at 4368. These in fact come quite close to Fraunhofer lines. We would especially like to point out the triplet at 3947 which, as we will see, belongs to one series with 777. According to this the middle line would be masked by an iron line. The two others, however, are somewhat stronger Fraunhofer lines with the right intensity relationships and of hitherto unknown origins. By far the strongest evidence for a coincidence with Fraunhofer's lines exists with the three lines at the extremity of red, because here the density of the lines is less, and thus a coincidence is far more significant.

Jewell<sup>1</sup> has investigated these three Fraunhofer lines as to their terrestrial origin and has found that they increase in intensity as the sun nears the horizon, and that their intensities show a greater variability than those of the oxygen band A. From this Jewell concludes that the Fraunhofer lines have their origin in water vapor in the atmosphere. It follows that their correspondence with oxygen lines must be accidental. We do not agree with this conclusion, since it seems improbable that both wavelengths and intensities in this relatively unpopulated area of the spectrum should coincide by sheer accident. There is also a further argument. As is shown below, the oxygen spectrum reveals definite regularities according to which we can predict certain values for the wavelength differences among the red oxygen lines. Now, Higg's photographs show the three Fraunhofer lines with greater accuracy than could be achieved in our own measurements of the red lines, and the differences in the wavelengths of the Fraunhofer lines agree even better with the predicted values than do the measurements made on oxygen itself. It follows from these observations that 1.) the lines of the solar spectrum are identical with the oxygen lines measured by us, and therefore 2.) that they cannot be lines produced by water vapor in the atmosphere. Jewell's observations show clearly that the lines of the solar spectrum are of terrestrial origin, but the proof that they are, in fact, produced by atmospheric water vapor seems far from clear to us. Thus we have no choice but to assume that the lines of the solar spectrum have their origin in the absorption of atmospheric oxygen, and that we are faced with the remarkable

1: Jewell, Astrophysical Journ. 5. Febr. 1937.

case in point, that is that oxygen in Geissler's tubes also emits the very same lines.

As for the coincidences with lines of the chromosphere, no conclusion can be reached. In the case of the two green triplets, the strong triplet at 616 should also appear for the sake of the continuity of the series. As long as this is not observed, the other coincidences must be regarded as accidental.

### § 3. THE SERIES OF THE OXYGEN SPECTRUM

In addition to the six triplets observed by Piazzzi Smyth, we have found seven other triplets of the same structure, which along with the first six form two series. In the case of three of them we were also able to measure all three components; in the case of the weaker triplets the weaker components merged, so that we were only able to measure the strongest component and the mean formed by the two weaker components. The differences in the frequency numbers of the three components of each triplet are, insofar as the accuracy of our observations allows for a conclusion, the same for all triplets. In the following table, the reciprocal values of the wavelengths, reduced to a vacuum, are indicated. The comma [i.e. decimal point] is placed in such a manner that these reciprocal values are equal to the total number of oscillations needed by the lightwaves to traverse the distance of 1 cm in a vacuum. The reduction to vacuum values is according to the method described by Kayser and Runge<sup>1</sup> in their study of dispersion in air. Although this reduction is not crucial in order to convince oneself of the constant in the frequency differences, it is desirable for some of the calculations that follow.

---

1) Kayser u. Runge, Abhandl. d. Berl. Akad. 1893.

A	B	C	A	B	C
Observed	Reduced to a vacuum	Difference	Observed	Reduced to a vacuum	Difference
4450.287	4454.77		4809.18	20818.84	
4454.756	4455.21	365	4802.88	20817.80	346
4458.900	4456.00	295	4801.08	20816.64	174
4158.415	4162.82		4778.54	20811.31	
4158.898	4163.15	373	4778.07	20810.12	281
4159.195	4163.55	210	4772.72	20809.06	154
4167.041	4167.72		4770.22	21389.68	
4168.965	4168.07	323	4770.84	21389.97	435
4175.371	4168.20	292	4655.54	21478.88	
5380.835	18758.65		4654.74	21477.57	360
5329.774	18757.80	374	4654.41	21479.00	152
5329.162	18759.54	215			
5020.31	19913.63		4590.07	21780.17	
5019.52	19916.73	315	4589.16d	21784.49	482
5018.96	19918.99	221	4577.54	21833.35	
			4576.97d	21842.50	415
4988.94	20119.50				
4988.04	20123.14	364	4523.70	22099.71	
4967.58	20125.01	187	4522.95d	22103.37	368

# KEY TO THE TABLE:

- A as observed
- B 1/ reduced to value in a vacuum
- C difference

With the first four triplets, the intervals between the components could be measured by use of the larger grid. Thus those values are more precise by far than those of the subsequent triplets. If one considers only the former, the following mean for the differences is obtained: 3.20 and 2.08. One can then adjust the three components of each triplet by weighting them in such a way that the above differences obtain, even as their center of gravity remains the same.<sup>1)</sup> The second column in the table below indicates the values that have been adjusted according to this method. The three components are weighted 3, 2, and 1 respectively, according to their order of intensity, which gives an approximation also of the exactitude of the measurements.

<sup>1)</sup> This procedure can be deduced from the method of least squares.

D	E	F	G	KEY TO TABLE:
Schwingungszahl	Korrigierte Schwingungszahl	Differenz	Entsprechende Differenz der Wellenlänge	<u>D</u> Frequency number
15454.57	15454.56	- 0.01	0.004	<u>E</u> Adjusted frequency number
15455.25	15455.26	+ 0.01	- 0.004	<u>F</u> Difference
15490.20	15490.34	- 0.04	- 0.017	<u>G</u> Corresponding difference in wavelength
15493.12	15493.15	+ 0.03	- 0.011	
15497.12	15497.25	- 0.03	- 0.011	
15498.12	15498.30	- 0.03	- 0.015	
15557.54	15557.50	- 0.04	+ 0.012	
15590.97	15591.00	+ 0.03	- 0.009	
15592.99	15593.08	+ 0.09	- 0.027	
15753.65	15753.68	+ 0.03	- 0.009	
15757.36	15757.25	- 0.01	+ 0.003	
15759.54	15759.16	- 0.08	+ 0.023	
19913.63	19913.38	- 0.25	+ 0.063	
19916.73	19917.93	+ 0.30	- 0.076	
19918.99	19919.16	+ 0.17	- 0.043	
20119.50	20119.44	- 0.06	+ 0.015	
20123.14	20123.14	0.00	0.000	
20125.01	20125.22	+ 0.21	- 0.052	
20813.84	20813.86	- 0.18	+ 0.042	
20817.30	20817.36	+ 0.06	- 0.014	
20819.04	20819.44	+ 0.40	- 0.093	
20941.31	20941.28	- 0.03	+ 0.007	
20943.12	20944.98	- 0.14	+ 0.032	
20946.66	20947.06	+ 0.40	- 0.091	
21473.82	21473.78	- 0.10	- 0.022	
21477.37	21477.48	- 0.09	- 0.020	
21479.09	21479.50	- 0.41	- 0.102	

The corrections one would have to make in the wavelengths in order to bring them to the same difference values lie entirely within the range of possible observational error. As for the four triplets where we were not able to measure the weaker two components separately, the difference for the frequency value as measured for the strongest component and the arithmetic mean of the two weaker ones should equal 4.74. But the arithmetic mean of the two weaker components cannot be observed when they appear merged, since the observed line tends towards the stronger of the two. One can estimate this deviation from the arithmetic mean by comparing measurements taken from photographic exposures where the weaker components of the other triplet have merged. Here, we measure the following:

<u>H</u>	<u>I</u>	<u>J</u>	KEY TO THE TABLE:
Gemessen	Arithm. Mittel	Differenz	
5019.28	5019.24	0.04	<u>H</u> Measured value
4892.29	4892.18	0.11	<u>I</u> Arithmetic mean
4772.96	4772.90	0.06	<u>J</u> Difference
4654.66	4654.58	0.08	
	mean	0.07	

When we assume that the wavelength as measured is also ca. 0.07 more than the arithmetic mean for the four triplets that could not be measured three times, then the frequency number which corresponds to this measured wavelength must be ca. 0.33 smaller. If the frequency difference for these triplets is also constant, then we can expect to find the difference between the frequency number of the strongest component and that of the measured center of the two others to be not 4.74 but closer to 4.41. In fact that difference was found to be 4.35, 4.32, 4.15, and 3.66, meaning only 0.06, 0.09, 0.26, and 0.75 less than was expected. Thus the correction for a uniform frequency difference can be made by adjusting the values for each pair by 0.03, 0.04, 0.13 and 0.38 respectively, which corresponds to a shift in wavelength of 0.007, 0.008, 0.027, and 0.078 angstroms. For the frequency numbers of the strongest components we would obtain the following:

21389.59  
21780.13  
21838.22  
22099.33

The 13 triplets are, as Piazzzi Smyth has already noted of the six triplets known to him, distributed over the spectrum in a regular order. They form, as is shown in the illustration at the end of this monograph, two series converging on the same point, similar to the two series of triplets observed by Kayser and Runge,<sup>1)</sup> in the spectra of magnesium, calcium, strontium, zinc, cadmium, and mercury.

#### ILLUSTRATION 2.

Oxygen triplet:

3947.48/3947.66/3947.76

Exposure made using  
large grid (enlarged)

1) Kayser u. Runge, Abhdt. der Berl. Akad. 1891; vgl. auch Rydberg, Kongl. svenska vetenskaps. akademiens handlingar. 23. Nr. 11.

For each of the two series one can represent the frequency numbers with considerable accuracy in the format

$$A - \frac{B}{n^2} - \frac{C}{n^3} \text{ or also as } A - \frac{B}{n^2} - \frac{C}{n^3}$$

where A, B, C are constants and n runs through the values 3, 4, 5,....

A has three separate values, corresponding to the three components of the triplets, the differences among them equal to the constants of the frequency differences 3.70 and 2.08, while B and C have only one value each for each series of triplets. B in any case has values which do not vary a great deal for the series of all elements, so that for the most part the two subseries are differentiated by the values of C. --In our calculations, we have to take only one of the components into account, e. g. the strongest one. Having found the formula for representing the strongest component, then formulas for the other components can be derived from it by simply adding the numbers 3.70 and 5.78 to A. At the same time one can demonstrate that the formulas for the two series differ mainly by the value of the constant C. The frequency numbers of the neighboring triplets of the two series result in differences approximately proportional by  $1/n^3$

Difference		
	Difference	$1/n^3$
3	745.99	0.70
4	460.08	0.15
5	296.05	0.08
6	187.02	0.05
7	114.10	0.03
8	74.10	0.02

This also shows that the format

$$A - \frac{B}{n^2} - \frac{C}{n^3}$$

will give us a better correspondence than the format

$$A - \frac{B}{n^2} - \frac{C}{n^3}$$

The frequency numbers of the stronger series are represented by the formulas:

$$\begin{aligned} 23207.93 &= 110387.7 n^{-2} - 4814 n^{-3} \\ 23211.63 &= 110387.7 n^{-2} - 4814 n^{-3} \\ 23213.71 &= 110387.7 n^{-2} - 4814 n^{-3} \end{aligned}$$

- 1) We have made the same observation regarding the formulas for the series in the spectrum of helium.

the weaker series is represented by the formulas:

$$23108.35 - 107387.1 n^{-2} - 63108 n^{-4}$$

$$23107.55 - 107387.1 n^{-2} - 63103 n^{-4}$$

$$23100.83 - 107387.1 n^{-2} - 63108 n^{-4}$$

where  $n$  runs through values 4, 5, 6, .... The value  $n = 3$  still gives us positive frequency numbers, but since these lie within the infrared range, we were unable to make any observations. The constants for the formulas are calculated by the method of least squares from the frequency numbers of the strongest components of each triplet, following the adjustment of values to identical frequency differences. In this we assigned the same weight to all frequency numbers, even though the smaller numbers are determined with far greater accuracy. It is especially desirable that the first constant of the formula, which gives the point from which the series originates, be determined as exactly as possible. The constant is, in any case, principally determined by the highest frequency numbers. Thus it is useful when these are assigned a greater weight than would be warranted by their accuracy. In the tables below the values resulting from the formulas are compared with the observed values:

<u>a</u> Stärkere Serie.	
<u>b</u> Stärkste Komponente	23207.03 - 110257.7 $n^{-2}$ - 48146 $n^{-4}$
Mittlere	23211.03 - 110257.7 $n^{-2}$ - 48146 $n^{-4}$
<u>c</u> Schwächste	23215.03 - 110257.7 $n^{-2}$ - 48146 $n^{-4}$

# KEY TO THE TABLES ON pp. 19-20:

	<u>d</u> Berechnete Schwingungszahl	<u>e</u> Beobachtete Schwingungszahl	<u>f</u> Differenz Berechnet - Beobachtet	<u>g</u> Differenz in Wellenlänge
4	16233.48	16233.32	+ 0.04	- 0.02
	16237.18	16237.23	+ 0.10	- 0.04
	16239.26	16239.38	+ 0.12	- 0.04
5	18753.01	18753.05	- 0.26	+ 0.08
	18757.81	18757.59	- 0.22	- 0.07
	18759.90	18759.54	- 0.13	+ 0.04
6	20119.82	20119.40	+ 0.18	- 0.04
	20123.02	20123.14	+ 0.12	- 0.03
	20125.10	20125.01	- 0.09	+ 0.02
7	20941.08	20941.31	+ 0.23	- 0.05
	20944.79	20945.12	+ 0.34	- 0.08
	20946.86	20946.06	- 0.20	+ 0.05
8	21473.72	21473.88	+ 0.16	- 0.03
	21477.42	21477.57	+ 0.15	- 0.03
	21479.50	21479.00	- 0.41	+ 0.00
9	21838.52	21838.38	- 0.17	+ 0.04
	21842.22	21842.50		
	21844.50			
10	22099.24	22099.71	- 0.47	- 0.10
	22102.34	22102.87		
	22105.2			

- a stronger series
- b strongest component
- c weakest component
- d calculated frequency no.
- e observed frequency no.
- f observed - calculated
- g corresponding difference in wavelength
- h weaker series

# h Serienformeln

a Stärkere Komponente:  $20164.85 - 107507.1 \cdot n^{-2} - 0.0019 \cdot n^{-4}$   
 Mittlere " :  $19717.71 - 107507.1 \cdot n^{-2} - 0.0019 \cdot n^{-4}$   
b Schwächere " :  $19709.63 - 107507.1 \cdot n^{-2} - 0.0019 \cdot n^{-4}$

n	<u>d</u>	<u>e</u>	<u>f</u>	<u>g</u>
	Berechnete Schwingungszahl	Beobachtete Schwingungszahl	Beobachtet— Berechnet	Entsprechende Differenz der Wellenlänge
4	13484.84	13484.87	- 0.27	- 0.11
	13485.1	13485.25	- 0.20	- 0.12
	13491.62	13491.80	- 0.18	- 0.17
5	15390.89	15390.94	- 0.04	- 0.01
	15390.99	15390.97	+ 0.02	- 0.20
	15392.08	15392.00	- 0.08	- 0.27
6	16913.71	16913.68	- 0.03	+ 0.02
	16917.11	16916.78	- 0.33	+ 0.18
	16919.10	16918.90	- 0.20	+ 0.12
7	20814.61	20813.84	- 0.77	+ 0.13
	20818.31	20817.30	- 1.01	- 0.23
	20820.30	20819.04	- 1.26	+ 0.31
8	21389.88	21389.62	- 0.26	+ 0.03
	21393.58	21393.97		
	21395.64			
9	21779.29	21780.17	+ 0.88	- 0.19
	21782.09	21784.49		
	21785.07			

The first constants in the formulas for the two series diverge relatively little from each other. The difference is 14.08, which equals a wavelength difference of 2.6 angstroms. From this one can safely assume that the two series originate at the same point. Accordingly they are called subseries, following the nomenclature adopted by Rydberg and by Kayser and Runge. We have called the stronger series the 1. subseries, the weaker series the 2. subseries. Rydberg has another series formula, according to which the frequency number equals

$$A - B/(n + \mu)^{-2}.$$

If one assigns suitable values to the three constants A, B,  $\mu$ , one can represent the frequency numbers with a degree of accuracy not substantially different from that achieved by Kayser and Runge's formula. In fact, the difference between the two formulas does not appear significant, provided one thinks of Rydberg's formula as developed from negative powers of n. The constant  $\mu$  can always be taken as lying between -0.5 and +0.5.



The smaller the proportion between  $\mu$  and  $n$ , the more one can neglect the subsequent members of the series as against the first ones. We have also calculated Rydberg's formula for the strongest line of the triplets, and find:

KEY:

- |  |              |
|--|--------------|
| 1. Nebenserie: $23207.96 - 111.396 \cdot \mu - 0.0021 \cdot \mu^2$ | 1. subseries |
| 2. " : $23200.64 - 109911.3 \cdot \mu - 0.1127 \cdot \mu^2$        | 2. subseries |

Deviations of the calculated values from observed values are given in angstroms:

1. subseries	2. subseries
-0.02	+0.03
-0.07	-0.13
-0.03	+0.03
-0.04	+0.13
-0.01	+0.04
+0.	-0.10
-0.02	

Both formulas approximate observed values somewhat better than do the formulas of Kayser and Runge. With the second subseries the difference is still worth noting, but with the first subseries it is negligible. Another factor favoring Rydberg's formula is that the first constants in the first and second subseries converge more closely. The points from which the two series originate according to these formulas are only 1.4 angstroms apart, and the difference between the two constants has been diminished.

Rydberg has stated his expectation, derived by analogy from the series of line-pairs in the spectra of the alkalis, that a main series of triplets accompanies every two subseries of triplets, and that the frequency numbers for this main series can be derived from the formula for the 2. subseries.<sup>1</sup> Yet, until now this main series has not been noted in any of the triplet spectra. In the spectrum of oxygen, however, Rydberg's prediction has been fulfilled on the whole. The connection is as follows: given that

$$J_c = B(n + \mu)^{-2} \quad (c = 1, 2, 3)$$

constitute the formulas for the 2. subseries of triplets, where  $n = 2$  is the least value for which the formula will produce a positive frequency number, which can still be brought about by altering the value of  $\mu$  by the appropriate

<sup>1</sup> Rydberg, Svenska vetensk. Akad. Handl. 23. Nr. 11. p. 39.

integer. Then, the formulas for the main series are:

$$A = B(n - \sigma)^{-2} \quad \sigma = 1, 2, 3,$$

where  $n$  runs through the values 1, 2, 3, ... and where, according to Rydberg,

$$\begin{aligned} (1) \quad A_1 &= B(1 - \sigma)^{-2}, \\ (2) \quad A &= B(1 - \sigma)^{-2} \end{aligned}$$

should be true. Then one should, according to Rydberg, be able to represent the frequency numbers of the 2. subseries by the formula:

$$B[(1 + \sigma_a)^{-2} - (n + \mu)^{-2}],$$

and those of the main series by the formula:

$$B[(1 + \mu)^{-2} - (n + \sigma_a)^{-2}].$$

At the same time, according to Rydberg, the intensity relationships of the three components should be the same for  $\alpha = 1, 2, 3$ . From formula (1) follows that the strongest and the weakest components in the main series should be the reverse of those in the subseries. Since  $\sigma = 1, 2, 3$  which, according to (1) ought to be proportional to  $A_\alpha$ , increases with increasing  $\alpha$  and therefore  $A_\alpha$  decreases with increasing  $\alpha$ . In the triplets of the main series of oxygen, therefore, the strongest line ought to have the largest frequency number and the weakest line should have the smallest number. Furthermore, the first triplet of the main series ( $n = 1$ ) must give us the same frequency differences as the triplets of the subseries, while the subsequent triplets rapidly converge.

Accordingly, the first two triplets of the main series should have the following frequency numbers:

	$\sigma = 1$	$\sigma = 2$
strongest component	12341.33	24371.72
middle component	12346.03	24377.04
weakest component	12350.81	24379.57

After larger frequency numbers there are in fact two strong triplets of the expected structure, i. e. the strong red triplet at the wavelength 777 and the strong triplet at 3947. These give the following frequency differences:

strongest component	12341.33	24371.72
middle component	12346.03	24377.04
weakest component	12350.81	24379.57

The frequency differences for these observed triplets fit the calculated values so well that any difference between them can be assigned to normal observational error. In the case of the red triplet, the distance between

the two weaker components might easily have been judged too large, since they were only visible separately when observed with the narrow aperture, which produces a reduced brightness making accurate measurement difficult. The center of these two weaker components should be more amenable to accurate measurements against the stronger component, since this difference could be measured at the larger aperture. In fact this distance as observed matches the calculated value quite exactly. The distances between the lines of the second triplet which could be photographed in the second order with the larger grid were also exactly as calculated. Therefore we unhesitatingly express our conviction that here for the first time we have observed a main series of triplets, and that Rydberg's link between the main series and the second subseries does indeed represent a certain approximation of demonstrable facts, as far as oxygen is concerned. Equation (1) appears to be fulfilled more exactly in this case than equation (2), which is also the case for the alkali spectra. The content of equation (1) can also be expressed in the following manner:

$$1 - \lambda_1 = 1 - B \cdot 10^{-8} \cdot \lambda_1^{-2}$$

or in values: the differences of the positions from which the main series and the subseries originate equal the frequency numbers of the first triplets of the main series. This is the way this law has been formulated by Schuster who had newly discovered it, without being aware of Rydberg's<sup>1</sup> monograph. It is interesting to note that the frequency numbers of the Fraunhofer lines, which appear to coincide with the lines of the first triplet of the main series, give the calculated differences quite exactly, even more exactly than do the oxygen lines measured by us. According to figures given in Higg's atlas the three lines show frequency differences of 3.69 and 1.97, while the triplets in the subseries give on the average 3.70 and 2.08. The second deviation equals a difference of 0.07 angstrom, which lies well within the margin of observational error. This confirms, as stated above, our conviction that the Fraunhofer lines owe their origin to oxygen.

The conclusive proof that the triplets at 777 and 3947 are components of the main series will come only when subsequent triplets of the series are observed. The next triplet should total 0.09 angstrom units and lie near 3334; the next one should be even narrower and lie close to 3117. We have not been able to locate these lines.

1) Rydberg. Nature 55. p. 209.

It is nevertheless possible that the decrease in intensity, which is even more pronounced in the main series than in the subseries, turns so severe at this point that the lines in question are not as yet detectable with our methods of exposure. Of the lines observed 3947 still had an energy great enough so that we would have expected further lines even given our methods of exposure.

Outside of the triplet series there are two other series of lines in the oxygen spectrum. In all probability all of these lines are in fact narrow pairs; the four brightest appear as double lines on our exposures, and we were able to measure the brightest among them as two separate lines. In every case a weaker component lies on the side of lower wavelengths. It is likely that the difference between the frequency numbers of the main line and both of its components is identical for all pairs; but we cannot say anything definite in this regard and are forced to also restrict our calculations to the main lines.

# KEY TO TABLE:

a Stronger Series.  
Schwingungszahl =  $21200,11 - 10700 n^2 - 40250 n^{-2}$

<u>b</u>	<u>c</u>	<u>d</u>	<u>e</u>	<u>f</u>
Beobachtete Wellenlänge	Berechnete Schwingungszahl	Beobachtete Schwingungszahl	Differenz	Entsprechende Differenz der Wellenlängen
4 7254,32	13791,36	13791,15	- 0,21	+ 0,11
5 6046,56	16382,57	16382,51	+ 0,06	- 0,05
6 5003,16	17996,70	17996,86	- 0,16	- 0,13
7 4290,17	18866,82	18866,72	- 0,10	- 0,01
8 3740,23	19425,52	19425,55	+ 0,03	- 0,23
9 3347,58	19803,44	19804,59	- 0,55	+ 0,14
10 3070,73	20075,43	20075,93	+ 0,50	- 0,12

- a Stronger Series:  
frequency number = ...  
b observed wavelength  
c calculated frequency no.  
d observed frequency number  
e difference  
f corresponding difference in wavelengths

g Schwächere Serie.  
Schwingungszahl =  $21210,98 - 110829,5 n^{-2} - 2455 n^{-3}$

<u>b</u>	<u>c</u>	<u>d</u>	<u>e</u>	<u>f</u>
Beobachtete Wellenlänge	Berechnete Schwingungszahl	Beobachtete Schwingungszahl	Differenz	Entsprechende Differenz der Wellenlängen
4 7002,48	14276,56	14276,79	+ 0,22	- 0,11
5 5958,75	16777,92	16777,49	- 0,44	+ 0,10
6 5512,92	18184,77	18184,27	- 0,50	+ 0,15
7 5275,25	18952,11	18951,23	- 0,88	+ 0,23
8 5130,70	19482,23	19483,20	+ 0,97	- 0,78
9 5037,84	19845,48	19846,81	+ 0,83	- 0,21
10 4973,05	20103,20	20102,59	- 2,31	+ 0,57

- g Weaker Series:  
frequency number = ...

Both formulas are calculated according to the method of least squares, in which all frequency numbers are assigned the same weight. This also gives the higher frequency numbers more importance than is warranted by their accuracy, but is nonetheless preferable since by this method the terminus of the series, the frequency numbers corresponding to  $n=\infty$ , can be determined with greater exactitude.

Following Rydberg's formula, we obtain for the same series the formulas:

$$21203.36 - 109366.7(n - 0.16191)^{-2}$$

$$21211.11 - 110846.7(n - 0.01093)^{-2}$$

The difference as compared to observed values is insignificant. At the same time one must say in favor of Rydberg's formulation once again that his first constants for both series as well as the second constants show less deviation than those in the formulations of Kayser and Runge.

According to the formulas, the two series originate close to the same point. They must therefore be regarded as subseries. Thus, the oxygen spectrum has two sets of subseries. It seems that there is also a second main series, which relates to the second pair of subseries in a way similar to the relationship of the first main series with the first pair of subseries. If we take the formula  $21203.36 - 109366.7(n - 0.16191)^{-2}$

from the one series, following Rydberg's law deriving from it the formula

$$A - 109366.7(n + \sigma)^{-2}$$

where

$$21203.36 = 109366.7(1 + \sigma)^{-2}$$

and

$$A = 109366.7(2 - 0.16191)^{-2}$$

then we obtain the following frequency numbers for  $n=1, 2, 3$ :

11165,10

22148,96

26375,15

The first number corresponds to a wavelength in the infrared region, in which we lack measurements. The following two lines, however, are not markedly different from the frequency numbers of the two strong lines at 4368.466 and at 3692.586:

calculated	22148,96	26375,15
observed	22860,23	27072,00
difference	-711	697

In the case of the first main series the calculated values for 820 and 947 were less than those observed. Therefore it is not impossible that we have here a second main series, although we did not succeed in finding the subsequent lines. It must also be emphasized that the frequency numbers calculated for the main series are derived from the frequency numbers of the stronger of the two subseries, whereas according to Rydberg the weaker subseries should have been used.

The overview of the six series given in the illustration at the end of this article shows great similarities with the six series in the spectrum of Cleveite gas.<sup>1</sup> Two subseries each and the main series belonging to them give us the picture of an alkali spectrum. In our work on Cleveite gas we spoke about our feeling that it was composed of two elements, corresponding to two groups of three series each. This conclusion must now be rejected, since the same reasoning could lead one to conclude that oxygen had two separate component elements.

#### § 4. THE SERIES SPECTRUM OF SULFUR

Sulfur exhibits a spectrum analogous to the compound line spectrum of oxygen. We equipped the Geissler tubes with a bulb-shaped end which we filled with concentrated sulfuric acid. The electrodes consisted of thin platinum plates and the tube remained connected to the U-shaped tube described above for the generation of oxygen. We heated the sulfuric acid in the bulb until it vaporized and some of the vapor condensed in the capillary part. When one waited until the water vapor produced at the same time was mostly absorbed, while running a stream of oxygen through the tube at the same time, then the spectrum described below appeared right afterwards. Provided the tube was set up using pure materials from the start, this was a pure spectrum, aside from the compound line spectrum produced by the oxygen. After some time it became strongly contaminated by the second oxygen spectrum, probably due to contamination of the sulfuric acid with organic compounds. The principal lines of the new spectrum also showed up when sulfur was heated in the tube and oxygen was introduced; secondly, when sulfuric acid was introduced. In both of these cases the band spectrum dominates, and it seems that the new spectrum is only produced in the presence of oxygen.

1) C. Runge u. F. Paschen, *Astrophysical. Journ.* Jan. 1-96.

It is best preserved with sulfuric acid and even then it improves in an oxygen atmosphere. The following table shows the observed wavelengths:

<u>a</u> Wellen- länge	<u>b</u> mittlerer Fehler	<u>c</u> Zahl Beobach- tungen	<u>d</u> Inten- sität	<u>e</u> Bemerkungen	<u>KEY TO THE TABLE:</u>	
4894.857			10	Die Abstände der drei Linien sind mit dem grossen Gitter gemessen und sind erheblich genauer als die Wellenlängen selbst.	<u>a</u>	wavelength
4895.690	0.03	3	8		<u>b</u>	mean error
4896.155			6		<u>c</u>	no. of observations
5275.41			1	Die Abstände der drei Linien sind mit dem grossen Gitter gemessen und sind erheblich genauer als die Wellenlängen selbst.	<u>d</u>	intensity
5275.81	0.03	3	8		<u>e</u>	remarks
5276.15			6		<u>f</u>	intervals of these three
5287.58		1	2	Die Linien stülft mit einer Verunreinigung zusammen, die vielleicht von Sauerstoff herrührt.	lines were measured with the larger grid and are much more precise than the wavelengths.	
5290.89	0.03		4		<u>g</u>	the same is true for these lines.
5295.56	0.05	3	4		<u>h</u>	this line coincides with an impurity, possibly stemming from oxygen.
5372.32	0.03	6	2		<u>i</u>	this weak line could only be determined to ca. 2 angstrom units.
5373.98	0.04	6	3			
5381.19	0.04	6	4			
5444.38	0.08	2	2			
5449.99	0.05	2	3			
5498.38	0.05	6	3			
5501.73	0.08	6	4			
5507.20	0.08	6	5			
5605.52	0.06	4	3			
5608.87	0.03	3	4			
5614.48	0.07	3	5			
5697.02	0.03	6	6			
5700.53	0.02	6	7			
5706.44	0.01	6	8			
5879.79	0.03	2	1			
5883.74	0.04	3	2			
5900.98	0.01	2	1			
6042.17	0.01	2	1			
6046.22	0.02	2	1			
6052.97	0.03	1	1			
6173.77	0.11	2	1			
6175.91	0.01	2	1			
6335.19		1	1			
6893.99		1	1			
6408.70	0.04	4	2			
6408.82	0.02	4	3			
6415.68	0.02	3	4			
6536.55	0.06	3	1			
6538.72	0.08	1	1			
6748.92	0.15	3	2			
6749.96	0.05	4	6			
6757.40	0.05	1	7			
7242.00			2	Diese schwache Linie konnte nur auf etwa 2 Angström genau bestimmt werden.		

## § 5. THE SERIES OF THE SULFUR SPECTRUM

The greater part of the lines listed here form two series of triplets, which show many analogs to those of the oxygen spectrum. The differences of the frequency numbers of the three components of each triplet are once again identical for all triplets, insofar as our observations allow such conclusions:

### KEY TO THE TABLE:

a	b	c	d
Beobachtete Wellenlänge	Schwingungszahl	Differenz	Bemerkungen
6787.40	14794.58	18.29	
6749.06	14812.87	11.29	
6743.92	14824.16		
6413.88	15382.37	17.90	
6405.32	15800.47	11.26	
6403.70	15611.73		
6032.97	16516.82	18.41	
6046.23	16384.78	11.12	
6042.17	16145.85		
5850.08	16670.17	18.29	
5853.74	16610.88	11.12	
5879.79	17110.78		
5706.11	17510.28	18.01	
5700.58	17337.28	10.97	
5697.02	17348.26		
5614.48	17506.28	17.81	
5608.87	17824.01	10.66	
5605.32	17824.70		
5507.20	18152.09	17.89	
5501.75	18170.38	11.24	
5498.38	18182.22		
5449.99	18843.04	18.23	
5444.58	18261.87		Dritte Componente nicht beobachtet.
			<u>e</u>
5381.18	18378.17	18.01	
5375.99	18598.18	10.94	
5372.82	18607.12		
5295.36	18877.50	17.74	
5290.89	18805.24	10.76	
5287.98	18906.00		



The mean values for the frequency differences are 18.15 and 11.13, when weighting is taken into account. One can now adjust the three components of each triplet by weighting them so that the frequency differences 18.15 and 11.13 obtain while the center of gravity of each triplet remains at the same point. The corrected frequency numbers are given in column two of the following table:

Beobachteter $f$ Schwingungs- zahl	Corrigirter $g$ Schwingungs- zahl	$h$ Differenz	Entsprechende Differenz der Wellenlänge	Mittlerer $\pm$ Fehler der $i$ beobachteten Wellenlänge
14704.58	14704.68	+ 0.05	- 0.02	0.05
14812.57	14812.78	+ 0.09	+ 0.04	0.08
14824.16	14823.91	- 0.25	+ 0.11	0.18
15582.57	15582.45	- 0.12	- 0.05	0.02
15600.57	15600.69	+ 0.12	- 0.07	0.02
15611.73	15611.73	0.00	0.00	0.00
16516.42	16516.42	- 0.12	- 0.05	0.02
16534.70	16534.70	- 0.17	- 0.07	0.03
16645.57	16645.70	+ 0.12	- 0.04	0.02
16678.07	16678.12	+ 0.05	- 0.02	0.01
16991.28	16991.27	- 0.01	+ 0.03	0.04
17002.75	17002.40	- 0.35	+ 0.13	0.05
17519.28	17519.28	- 0.05	+ 0.02	0.01
17537.29	17537.08	+ 0.09	- 0.03	0.02
17548.29	17548.51	+ 0.25	- 0.08	0.03
17806.23	17805.84	- 0.39	+ 0.12	0.07
17823.54	17823.99	+ 0.45	+ 0.02	0.03
17834.70	17835.12	+ 0.42	- 0.13	0.03
18153.02	18152.99	- 0.03	- 0.04	0.03
18170.95	18171.11	+ 0.16	- 0.04	0.03
18182.22	18182.24	+ 0.02	- 0.01	0.05
18843.64	18843.66	+ 0.02	- 0.01	0.05
18361.57	18361.81	+ 0.06	+ 0.02	0.03
18578.17	18578.04	- 0.13	+ 0.04	0.04
18596.15	18596.19	+ 0.04	- 0.00	0.04
18607.12	18607.32	+ 0.20	- 0.06	0.05
18877.50	18877.15	- 0.35	+ 0.10	0.03
18895.24	18895.30	+ 0.06	- 0.02	0.03
18908.00	18908.48	+ 0.48	- 0.12	-

# KEY TO THE TABLE:

- $f$  observed frequency number
- $g$  corrected frequency number
- $h$  difference
- $i$  corresponding difference in wavelength
- $j$  mean<sup>1)</sup> error in observed wavelength

- 1) Concerning the mean error, the observations regarding the oxygen spectrum are also in order here. Given the small number of measurements, the exactitude of a wavelength is to be judged less by the individual mean errors than by the mean error taken as a whole.

As is shown by the illustration at the end of this article, the triplets can be arranged in two series, which decrease in intensity as the frequency numbers increase, and originate at the same point. In other words, they have the characteristics of subseries. We have observed six triplets of the stronger of the two series, which we call the 1. subseries, while we have found only four of the weaker series, which we call the 2. subseries. The frequency numbers can once again be represented by a formula:

$$f = B + n \cdot \Delta f$$

where the constant B has approximately the same value as in all other series. In the following, the values of the formulas are compared with our observed values.

The formula is calculated in such a way that it corresponds most closely to the frequency numbers corrected to the constant frequency difference by the method of least squares. All frequency numbers are assigned equal weight at the same time.

The formulas are derived from the frequency numbers of the first three triplets, corrected to identical frequency differences, without equalization. Inclusion of the fourth triplet would alter nothing in our calculations.

The formulas of the two series show by the close correspondence of their first constants that the two series originate very close to the same point.

For smaller values of n the formula of the first series gives us two more triplets which fall in the infrared range, where we made no observations. The formula for the second series also gives us two more triplets, of which one should lie around 770 and thus should be still barely visible. We have searched for it but could not discover it. At that it is quite possible that the lines escaped us due to the smaller intensity of the second series and the decreased sensitivity of the eye in this range of the spectrum.

#### ILLUSTRATION 3.

Sulfur triplet:

4694.4/4695.7/4696.5

Exposure made using  
the large grid (enlarged)

# KEY TO THE TABLES:

- a 1. subseries
- b strongest line
- c middle line
- d weakest line
- e frequency number as calculated
- f frequency number as observed
- g difference
- h corresponding difference in wavelengths
- i 2. subseries

## a 1. Nebenserie.

b Stärkste Linie:  $20087.89 = 109398 n^{-2} = 113356 n^{-3}$   
c Mittlere .. :  $20103.04 = 109398 n^{-2} = 113356 n^{-3}$   
d Schwächste .. :  $20116.17 = 109398 n^{-2} = 113356 n^{-3}$

<u>e</u>	<u>f</u>	<u>g</u>	<u>h</u>
Berechnete Schwingungszahl	Beobachtete Schwingungszahl	Differenz	Entsprechende Differenz der Wellenlängen
18744.52	18744.52	- 0.00	- 0.00
18742.87	18742.87	- 0.00	- 0.00
18741.59	18741.59	- 0.00	- 0.00
18741.17	18741.17	- 0.00	- 0.00
18740.78	18740.78	- 0.00	- 0.00
18740.43	18740.43	- 0.00	- 0.00
18740.10	18740.10	- 0.00	- 0.00
18739.78	18739.78	- 0.00	- 0.00
18739.48	18739.48	- 0.00	- 0.00
18739.20	18739.20	- 0.00	- 0.00
18738.93	18738.93	- 0.00	- 0.00
18738.68	18738.68	- 0.00	- 0.00
18738.44	18738.44	- 0.00	- 0.00
18738.21	18738.21	- 0.00	- 0.00
18737.99	18737.99	- 0.00	- 0.00
18737.78	18737.78	- 0.00	- 0.00
18737.58	18737.58	- 0.00	- 0.00
18737.39	18737.39	- 0.00	- 0.00
18737.21	18737.21	- 0.00	- 0.00
18737.03	18737.03	- 0.00	- 0.00
18736.86	18736.86	- 0.00	- 0.00
18736.69	18736.69	- 0.00	- 0.00
18736.52	18736.52	- 0.00	- 0.00

## i 2. Nebenserie.

b Stärkste Linie:  $20079.37 = 108744.5 n^{-2} = 18268 n^{-3}$   
c Mittlere .. :  $20096.52 = 108744.5 n^{-2} = 18268 n^{-3}$   
d Schwächste .. :  $20107.65 = 108744.5 n^{-2} = 18268 n^{-3}$

<u>e</u>	<u>f</u>	<u>g</u>	<u>h</u>
Berechnete Schwingungszahl	Beobachtete Schwingungszahl	Differenz	Entsprechende Differenz der Wellenlängen
15582.45	15582.57	- 0.12	- 0.05
15600.80	15600.47	- 0.13	- 0.05
15611.73	15611.73	0.00	0.00
15673.12	15673.07	- 0.05	- 0.02
15691.27	15691.18	- 0.09	- 0.03
15702.40	15702.75	- 0.35	- 0.10
15805.54	15805.22	- 0.32	- 0.12
15822.89	15824.03	- 0.05	- 0.02
15935.12	15934.70	- 0.42	- 0.13
15948.56	15948.64	+ 0.08	- 0.02
15961.71	15961.57	+ 0.14	- 0.05
15972.54	15974.70	- 1.59	- 0.55

By analogy with the oxygen spectrum, one would expect an additional main series of triplets, in which the frequency differences do not remain constant but draw closer together from triplet to triplets as the frequency numbers increase. In this, according to Rydberg's law, the strongest component would have the smallest frequency number in each triplet, the reverse of the situation in the subseries. According to Rydberg the formula of this series could be calculated from that of the 2. subseries, in the manner indicated above for the oxygen spectrum. In Rydberg's formulation, the formula for the frequency numbers of the 2. subseries is:

$$\begin{aligned} \text{strongest line: } & 20075.07 - 105868.5/n^2 - 0.070451/n^4 \\ \text{middle line : } & 20097.19 - 105868.5/n^2 - 0.070451/n^4 \\ \text{weakest line : } & 20108.23 - 105868.5/n^2 - 0.070451/n^4 \end{aligned}$$

From this we derive the formula for the main series:

$$\begin{aligned} \text{strongest line: } & 29515.56 - 105868.5/n^2 + 0.32852/n^4 \\ \text{middle line : } & 29515.56 - 105868.5/n^2 + 0.32747/n^4 \\ \text{weakest line : } & 29515.56 - 105868.5/n^2 + 0.32688/n^4 \end{aligned}$$

For  $n=2$  the triplet falls in the infrared range, but for  $n=3$  we get the frequency numbers:

		difference
strongest line:	19639,05	
middle line :	19682,34	6.21
weakest line :	19679,05	3.79

With the oxygen spectrum the numbers so calculated give only a rough approximation of the actual values. Only their differences corresponded well with the differences of the actual values. The actual frequency numbers were considerably larger. If we suspect a similar case here, it is not improbable that the strong triplet at wavelength 469 belongs to the main series. It is true that the frequency numbers exceed the calculated values by even more than in the case of the corresponding oxygen lines, yet the frequency differences fit the calculated values quite well.

	<u>Wavelength</u>	<u>Frequency no.</u>	<u>Difference</u>
strongest line:	469,807	21290,82	0,00
middle line :	470,000	21290,97	1
weakest line :	470,455	21291,06	3,81

Rydberg's derivation of the formula for the main series contains two assumptions, as explained above, and these can be regarded separately. the first contains only a rough approximation of actual data. The other one is well demonstrated in other spectra as well, and can be stated as follows: the difference between the frequency numbers of the ends of the main and subseries equals the frequency numbers of the first member of the main series. If one considers this assumption by itself, then one has a constant for the determination of the main series formula and one can use observed values to calculate the formula:

frequency number of the strongest line:	$31123.00 - 108868.5 (n - 0.32552)^{-2}$
frequency number of the middle line :	$31123.00 - 108868.5 (n - 0.32747)^{-2}$
frequency number of the weakest line :	$31123.00 - 108868.5 (n - 0.32933)^{-2}$

These formulas now give for the following value of n the wavelengths (in air):

3949.54

3948.90

3950.25

which we were no more able to observe than the corresponding lines of the oxygen spectrum. The intensity in the main series must therefore also be decreasing rapidly at higher frequency numbers, if this assumption regarding the main series is correct.

We think it quite probable that the sulfur spectrum also has analogs for the other three series of the oxygen spectrum. At the same time we did not succeed in demonstrating their existence. The strong triple line at 5279 possibly corresponds with the strong oxygen line at 4368. This would then have to be a narrow triplet, so narrow that it would be very difficult to separate the components. Then the two subseries belonging to 4368 would also have to consist of triplets. A comparison of the frequency differences of the other oxygen- and sulfur-triplets shows, in fact, that the frequency differences of 3.70 and 2.08 with oxygen increase to 18.15 and 11.13 with sulfur, that is by a ratio of 1 to 5. With the alkalis the frequency difference increases from element to element proportional to the square of the atomic weights. Here the increase is somewhat more pronounced, since the squares of the atomic weights of oxygen and sulfur are in the proportion 1 to 4.

## § 6. THE SERIES SPECTRUM OF SELENIUM

Selenium also has a spectrum analogous to the compound line spectrum of oxygen. If one puts selenic acid instead of concentrated sulfuric acid<sup>1)</sup> into the bulb of the Geissler tube, treating it in the manner described on p. 669 above [p. 26 of the translation], the series spectrum of selenium appears. The selenic acid must be heated to a somewhat higher temperature than the sulfuric acid before the vapor begins to condense in the capillaries and the spectrum becomes bright. On the other hand, the spectrum remains good for a longer period than that of sulfur. As with the generation of a sulfur spectrum, the presence of an oxygen atmosphere appears to favor the generation of a selenium spectrum. Again as with oxygen and sulfur, the lines of the selenium spark spectrum can be seen at the same time. We were able to observe many, though not all, of the lines of the selenium spark spectrum described by Plücker and Hittorf. These are not listed in the table below. Our primary concern was that selenium spectrum to which the triplets belong. Only this latter spectrum was visible from time to time, along with the lines of oxygen and hydrogen. But we did not retain the tubes in this state for any length of time. Therefore we did not obtain a pure spectrum on our photographs, which needed a longer exposure due to the lesser intensity. Among the red lines we were only able to measure the stronger ones. Only these are listed in our table, along with some weaker lines lying next to the measured lines, which latter could then be estimated without a micrometric measurement.

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<sup>1)</sup> We concentrated the commercially obtained dilute selenic acid by careful evaporation until it no longer gave off water vapor in a vacuum.

<u>a</u>	<u>b</u>	<u>c</u>	<u>d</u>	<u>e</u>
3731.27	0.07	1	1	Die Differenzen dieser drei Linien, die mit dem grossen Gitter gemessen werden konnten, sind von sehr geringer Grösse, die absolute Werte <u>f</u>
3734.27	0.03	1	10	Dasselbe gilt von diesen drei Linien. <u>g</u>
3737.32	0.15	3	3	
3737.3	0.11	3	3	
3738.34	0.05	3	1	
3738.35	0.03	2	3	
3738.32	0.01	2	3	
3738.35	0.03	2	3	
3738.32	0.07	2	3	
3738.35	0.05	4	4	
3738.35	0.03	4	3	
3738.35	0.03	4	7	
3738.35	0.00	3	2	Abst. v. d. vorigen Linie geschätzt. <u>h</u>
3738.32	0.04	4	7	
3738.30	0.06	2	1	
3738.10	0.05	4	2	
3738.33	0.10	3	2	
3738.33	0.06	4	2	
3738.10	0.03	2	2	
3738.40	0.02	1	2	
3738.12	0.02	4	4	
3738.17		1	1	Abst. v. d. v. d. Linie geschätzt. <u>h</u>
3738.17		1	1	Abst. v. d. folgenden Linie geschätzt.
3738.17	0.03	1	1	
3738.17	0.17	1	2	
3738.32	0.00	1	1	
3738.31	0.00	1	2	
3738.37	0.10	1	1	
3738.36	0.06	4	4	
3738.28	0.09	2	3	
3738.34	0.06	2	2	
3738.10		1	1	Abst. v. d. benachb. Linie geschätzt. <u>h</u>
3738.31	0.07	4	1	
3738.31		1	1	Abst. v. d. folgenden Linie geschätzt. <u>h</u>
3738.31	0.03	4	3	
3738.32	0.10	1	3	
3738.35	0.06	3	3	
3738.29	0.03	2	1	
3738.35	0.07	3	3	
3738.28	0.24	3	3	
3738.36	0.06	3	4	Vielleicht doppelt. <u>i</u>
3738.34	0.12	3	3	
3738.25	0.09	3	3	
3738.14	0.06	3	3	

# Key:

- a wavelength
- b-mean error
- c number of observations
- d intensity
- e remarks
- f The differences of these three lines, which could be measured with the large grid, are substantially more exact than the absolute values.
- g the same is true for these three lines
- h distance estimated from preceding line
- i perhaps a double line.

It is not beyond the range of possibility that some of the weaker among the lines listed here belong to the spark spectrum. Nevertheless, the greater part forms a series spectrum of triplets that do not appear in the spark spectrum, one that is analogous to both of the described spectra of sulfur and oxygen.

The constants of the differences between the frequency numbers of the triplets lines cannot be demonstrated as clearly with selenium as with the elements of lesser atomic weight. It appears that the components of these triplets are accompanied in part by weak companions, and that these and not the principal lines give us the constant frequency differences. Similar features have been observed with the 1. subseries of calcium, strontium, zinc, cadmium, and mercury. These weak companions are, however, easy to miss and cannot be measured accurately. Therefore we would like to avoid the ready conclusion from the deviations from the constant frequency difference, which would suggest that the complete and exact measurement of of the weaker components would not result in a constant here also.

<u>a</u> Wellenlänge	<u>b</u> Frequenznummer	<u>c</u> Differenzen
7014.1	14156.17	
7014.24	14252.94	103.50
7016.84	14259.76	47.47
6994.964	14300.31	40.55
6746.65	14818.15	
6747.29	14918.45	103.90
6749.75	14921.81	48.18
6750.72	14966.63	44.82
6325.51	15803.95	
6325.4	15804.98	103.55
6284.51	15907.50	103.64
6284.19	15908.62	
6282.54	15910.27	
6269.23	15946.45	45.27
6268.26	15953.89	43.62
6177.87	16182.41	
6133.51	16236.17	103.76
6121.95	16330.22	44.05
5962.08	16768.10	
5961.7	16769.17	104.05
5925.31	16872.15	103.50
5925.13	16872.67	45.18
5909.49	16917.38	44.86

# KEY TO THE TABLE:

- a wavelength
- b frequency number
- c differences



<u>a</u> Wellenlänge	<u>b</u> Schwingungszahl	<u>c</u> Differenzen
5875.88	17005.41	101.13 44.62
5843.10	17109.54	
5827.90	17154.16	
5755.52	17375.92	106.41 102.75 108.12
5752.31	17379.58	
5718.5	17482.33	
5718.28	17482.00	
5705.15	17523.15	44.20
5703.86	17527.20	
5700.02	17535.09	101.25 41.71
5674.55	17641.67	
5672.02	17686.06	
5628.74	17832.07	101.25
5617.1	17896.57	

# KEY TO THE TABLE:

- a wavelenegth
- b frequency number
- c differences

It is not practicable to correct the numbers to equal frequency differences, as was done with the oxygen- and sulfur-triplets, since with the weak companions one never knows which line should be adjusted and how. All the same one can become convinced that the triplets form two series. In the illustration at the end of this article they are graphed, where, due to the small scale employed, the weak companions are not indicated. The dotted lines are not as observed, but drawn to better show the symmetry with the other lines.

In order to show that both series can be represented by formulas, which show all the characteristics of series formulas, it is enough to take one line from each triplet. With triplets that do not show companions we chose the longest wavelength, with the others the companion having the longest wavelength since it seems that the companions are the ones that give a constant frequency difference. Because of the uncertainty concerning the companions, the formulas are not equalized.

The frequency number that is the third from the last, 17794.91, matches the wavelength 5618.05. The other two components of the triplet should be

1) The third line was not observed.

a Erste (stärkere) Nebenserie.

b Schwingungszahl =  $19288.54 - 108900.0 n^{-2} - 94293 n^{-4}$

<u>n</u>	Berechnete <u>c</u> Schwingungs- zahl	Beobachtete <u>d</u> Schwingungs- zahl	<u>e</u> Differenz	<u>f</u> Bemerkung
5	14156.17	14156.17	0.00	Zur Berechnung der Constanten benutzt.
6	15804.98	15804.98	0.00	
7	16769.17	16769.17	0.00	
8	17380.80	17379.58	- 1.22	
9	17792.74	17794.91	- 2.17	<u>g</u>
10	18083.24	18082.60	- 0.64	
11	18295.60	18293.89	- 1.70	

h Zweite (schwächer) Nebenserie.

b Schwingungszahl =  $19286.72 - 111959.6 n^{-2} - 1227 n^{-4}$

<u>n</u>	Berechnete <u>c</u> Schwingungs- zahl	Beobachtete <u>d</u> Schwingungs- zahl	<u>e</u> Differenz	<u>f</u> Bemerkungen
5	14818.15	14818.15	0.00	Zur Berechnung der Constanten benutzt.
6	16182.41	16182.41	0.00	
7	17005.41	17005.31	0.00	
8	17539.75	17538.09	- 1.66	

KEY TO THE TABLES:

- a first (stronger) triplet  
b frequency number  
c calculated frequency no.  
d observed frequency no.  
e difference  
f remark  
g used for computing the constants  
h second (weaker) triplet

still strong enough in order to be noticeable, but they fall into one of the green oxygen bands. Presumably 5618.05 also has a weak companion of smaller wavelength. That would explain the unsystematic deviation of this line from the formula. The last frequency number belongs to the wavelength 5464.82. here the other two components of the triplet could no longer be observed. The line 5416.94 (intensity 1) frequency number 18455.57 (observed once) also belongs perhaps to the subsequent triplets, since calculation gives us a frequency number 18455.72. The line could also be due to contamination, however.

The two series of lines falling into the infrared range correspond to the smaller values of  $n$ , for which we have no observed values.

In order to search for a main series in the selenium spectrum, we have calculated the 2. subseries according to Rydberg's formula:

$$\text{Frequency number} = 19286.76 - 111963.0 n^{-2} + 9,00556 n^{-4}$$

If one assumes that the frequency differences of two neighboring components of a triplet are in the mean at 103.71 and 44.55, then the other two components can be represented by the following formula:

$$19390.47 - 111963.31n + 0.005561n^2$$

$$19435.02 - 111963.31n + 0.005561n^2$$

From this, according to Rydberg, one can find the formulas for the main series:

$$\frac{111963.31}{200000} = 0.55981655$$

where  $a_1, a_2, a_3$  are to be determined in such a manner that the second terminus  $111963.31n - a_2$  equal to the termini 19286.76, 19390.47, and 19435.02 becomes the formula for the 2. subseries.

In this manner one obtains the formulas:

strongest line: frequency number =  $27833.80 - 111963.31n + 0.005561n^2$   
middle line : frequency number =  $27833.80 - 111963.31n + 0.402051n^2$   
weakest line : frequency number =  $27833.80 - 111963.31n + 0.400105n^2$

For  $n=2$  we get wavelengths falling in the infrared range. For  $n=3$ , on the other hand, we obtain the frequency numbers:

difference

strongest line: 19286.76  
middle line: 19390.47  
weakest line: 19435.02

The numbers so calculated represent a very rough approximation in the cases of oxygen and sulfur. Only their differences gave a good correspondence with actual values. Actual frequency numbers were substantially higher. Thus it seems very probable that the strong triplet at 474 belongs to main series. We have here:

KEY:

		<u>d</u> Wellenlänge	<u>e</u> Schwingungszahl	Differenz	<u>f</u>
<u>a</u> Stärkste	Linie:	4731.02	21131.19	36.77	<u>a</u> strongest line
<u>b</u> Mittlere	" :	4739.23	21094.42	14.37	<u>b</u> middle line
<u>c</u> Schwächste	" :	4742.52	21080.05		<u>c</u> weakest line
					<u>d</u> wavelength
					<u>e</u> frequency number
					<u>f</u> difference

The frequency differences and the relative intensities fit the laws of Rydberg. The strongest component, which has the greatest wavelength in the subseries, here has become the shortest and the weakest has become the longest.

This is still not a sufficient final proof for the existence of a main series, since for that one would have to observe the other members of that series. One would expect the next member at ca. 400, and the intervals of the wavelengths should be at ca. 2.7 and 1.2 angstroms. We have not been able to observe this triplet. Thus, if the supposition regarding a main series is correct, the intensities would have to fall extraordinarily fast from member to member, otherwise the next member could not escape detection.

We can say nothing definite about whether the strong selenium triplet at 537 is in fact an analog of the strong oxygen line 4368 and the sulfur triplet at 528. It appears likely, given the general distribution of the data, as shown in the illustration at the end of this article. Yet, we would expect smaller frequency differences. Also their relative position shows no similarities with the components of the sulfur triplet at 528.

The frequency differences in the triplets of the subseries behave in relation to those of oxygen and sulfur, roughly speaking, as do the squares of their respective atomic weights.

#### KEY TO THE TABLE:

- a frequency difference
- b atomic weight
- c square of the atomic weight divided by the frequency difference

	<u>a</u>	<u>b</u>	<u>c</u>
O	3,70 und 2,08	16	69 und 123
S	15,15 " 11,13	32,06	37 " 92
Se	103,7 " 44,07	79,07	60 " 140

#### ILLUSTRATION 4.

Selenium triplet:

4731 / 4739 / 4742

exposure using large grid  
(enlarged)

Similar has been observed regarding the line pairs in the spectra of the alkalis, and in the triplets of the spectra of magnesium, strontium, calcium, and of zinc, cadmium, and mercury.

At the same time there is a regularity in that the series as a whole of O, S, and Se move towards the side of lower frequency numbers with the increase in atomic weights, a fact also observed in the series spectra of other chemically related elements.

Thus it is shown that oxygen, sulfur, and selenium all three have an analogous spectrum, for which we have used the name "series spectrum," in place of the name "compound line spectrum" used by Schuster.

We have also attempted to produce the spectrum of tellurium in the Geissler tubes. Following the analogy with the circumstances in which the series spectra of sulfur and selenium appear, we placed telluric acid, which Professor Seubert was kind enough to prepare for us, in the bulbous end of the Geissler tube. We treated it just as we treated selenic acid and sulfuric acid, but it soon became clear that the temperatures to which one can subject an ordinary glass tube (ca. 500°C) are not sufficient to vaporize telluric acid to the point that it would condense in the capillaries. We observed no tellurium lines in this attempt.

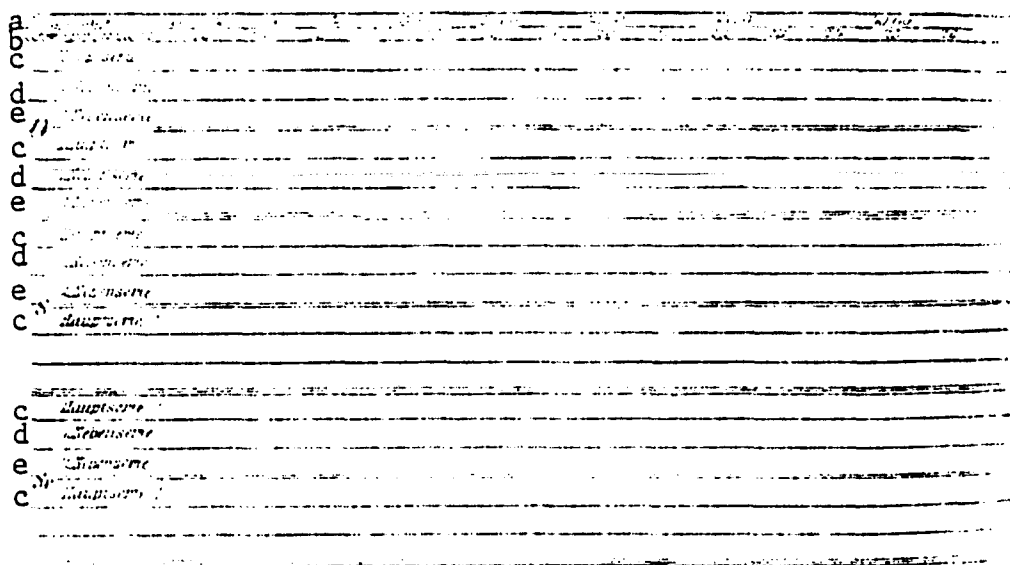


Fig. 5.

KEY TO ILLUSTRATION:

- a wavelength
- b frequency number
- c main series
- d 1. subseries.
- e 2. subseries

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